

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

0 357 295  
A2

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 89308329.5

(51) Int. Cl.<sup>5</sup>: C10G 49/04

(22) Date of filing: 15.08.89

(30) Priority: 19.08.88 JP 206194/88  
13.09.88 JP 229246/88  
13.09.88 JP 229247/88  
08.09.88 JP 225099/88  
19.09.88 JP 234000/88

(43) Date of publication of application:  
07.03.90 Bulletin 90/10

(84) Designated Contracting States:  
BE DE FR GB NL

(71) Applicant: SUMITOMO METAL MINING  
COMPANY LIMITED  
11-3, Shinbashi 5-chome Minato-ku  
Tokyo 105(JP)

(72) Inventor: Takahashi, Yasuhito  
2-1-10, Saginumadai  
Narashino City Chiba Prefecture(JP)  
Inventor: Kawaguchi, Tomio  
1-37-9, Matsugaoka  
Funabashi City Chiba Prefecture(JP)  
Inventor: Sakai, Shigeru  
3-18-35, Nakakokubun  
Ichikawa City Chiba Prefecture(JP)

(74) Representative: Hartley, David et al  
Withers & Rogers 4 Dyer's Buildings Holborn  
London, EC1N 2JT(GB)

(54) Catalysts for hydrotreating of hydrocarbons and methods of preparing the same.

(57) Disclosed are catalysts for hydrotreating hydrocarbons and methods for preparing the same, and the catalyst is composed of a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium, at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table and at least one organic compounds selected from mercapto-carboxylic acids of formula HS-(CH<sub>2</sub>)<sub>n</sub>-COOR (where n is 1 to 3; R is H, alkali metal, alkaline earth metal or ammonium group or alkyl group with 1-10 carbons), thio-acids of formula R'-COSH (where R' is monovalent hydrocarbon with 1-15 carbons), amino-substituted mercaptans of formula H<sub>2</sub>N-R''-SH (R'' is divalent hydrocarbon with 1-15 carbons), dimercaptans of formula HS-R'''-SH (R''' is same as above) and mercapto-alcohols of formula (RaS-R''-(OH)<sub>n</sub> (where R'' is hydrocarbon with 1-15 carbons; Ra is H or alkyl group with 1-2 carbons; and n is 1-2), and optionally phosphoric acid. The catalyst requires neither presulfurization nor heat-treatment and can directly be applied to hydrotreating hydrocarbons.

EP 0 357 295 A2

## CATALYSTS FOR HYDROTREATING HYDROCARBONS AND METHODS OF PREPARING THE SAME

FIELD OF THE INVENTION

The present invention relates to catalysts for hydrotreating hydrocarbons and methods of preparing the same.

BACKGROUND OF THE INVENTION

In a so-called hydrotreatment of hydrocarbons where a hydrocarbon oil is hydrogenated, desulfurized, denitrogenated or decomposed in the presence of hydrogen, a catalyst composed of at least one metal selected from metals of Group VI of the Periodic Table and metals of Group VIII of the Periodic Table, as an active component, as carried on an inorganic oxide carrier such as alumina ( $\text{Al}_2\text{O}_3$ ), silica-alumina ( $\text{SiO}_2\text{-Al}_2\text{O}_3$ ), titania ( $\text{TiO}_2$ ) or the like is employed. As the metal of Group VI, molybdenum (Mo) and tungsten (W) are well utilized for the purpose; and as the metal of Group VIII, cobalt (Co) and nickel (Ni) for the purpose.

Such metal is generally carried on the carrier in the form of an oxide thereof, which, however, is inactive as it is. Accordingly, the catalyst is required to be activated by presulfurization thereby to convert the metal oxide into the corresponding sulfide prior to being applied to hydrotreating reaction.

As a conventional means for such presulfurization which has hitherto been effected in general, a sulfurizing agent is introduced into the catalyst layer together with hydrogen, after the catalyst has been filled in a reactor where hydrotreating a hydrocarbon oil is to be effected. The operating condition for presulfurization varies in accordance with the hydrotreating process and with the sulfurizing agent used. For instance, where hydrogen sulfide is used as the sulfurizing agent, the compound is incorporated into hydrogen in an amount of from 0.5 to 5 % by volume or so, and the hydrogen sulfide-containing hydrogen is applied to the catalyst in an amount of from 1000 to 3000 liters per liter of the catalyst (as calculated under the condition of normal temperature and normal pressure) and the presulfurization is effected at  $180^\circ\text{C}$  or higher (generally  $250^\circ\text{C}$  or higher). Where carbon disulfide, normal-butyl mercaptan, dimethyl sulfide, demethyl disulfide or the like is used as the sulfurizing agent, the compound is diluted with a light hydrocarbon oil and is applied to the catalyst under the condition of a temperature of from  $250^\circ\text{C}$  to  $350^\circ\text{C}$ , a pressure of from 20 to 100  $\text{kg/cm}^2$ , a liquid space velocity of from 0.5 to 2.0  $\text{hr}^{-1}$ , and a hydrogen/oil ratio of from 200 to 1000 N-liter/liter.

After completion of such presulfurization, the reaction system is substituted by a raw material oil which is actually to be processed and the intended hydrotreatment is started with the thus activated catalyst. As the presulfurization has a significant influence on the success or not of the hydrotreatment to follow, pertinent selection of the materials to be employed in the process and careful operation of the process are required. Where a diluting agent is used, for instance, the agent must be a hydrocarbon oil free from olefins since olefins, if contained in the diluting agent, would form a polymer product and the product would poison the hydrotreating catalyst. The catalyst metal would be passivated, when reacted with hydrogen at a high temperature to be reduced. Accordingly, in order to prevent such passivation, it is necessary to use an excess amount of the sulfurizing agent, and the proportion of the sulfurizing agent and hydrogen must be maintained properly. Further, although such presulfurization is generally carried out for several days, it is not automated in most cases as the operation is a temporary one. In addition, the pre-sulfurization process requires some complicated treatment which is different from conventional one so that the labour load of the operators is extremely noticeable. Under the situation, omission of the pre-sulfurization step or at least reduction of the complicated operation of the step has been one problem in this technical field.

Recently, one method has been proposed, which could meet the request.

The method is directed to presulfurization of an active metal-carried catalyst by impregnating the said catalyst with a polysulfide of a general formula  $\text{R-S}(n)\text{-R}'$ , where  $n$  represents an integer of from 3 to 20, and R and R' each represent a hydrogen atom or an organic group having from 1 to 150 carbon atoms per one molecule, and heat-treating the thus impregnated catalyst under the condition of a temperature of  $65$  to  $275^\circ\text{C}$  and a pressure of 0.5 to 70 bars and in the absence of hydrogen gas (Japanese Patent Application Laid-Open No. 61-111144).

In accordance with the method, the polysulfide as introduced into the catalyst sulfurizes the active metal

by heat-treatment. Accordingly, where the above-mentioned presulfurization is carried out in a reactor, with a sulfurizing agent nor diluting agent is necessary and the operation is easy. In addition, the above-mentioned pre-sulfurization may also be effected even outside the reactor. In such case, the presulfurized catalyst may be applied to the reactor whereupon the intended hydrotreatment may immediately be started thereafter.

However, the amount of the polysulfide to be used in the said method is a stoichiometrical amount necessary for sulfurizing the whole active metal oxide (for example, CoO, MnO<sub>3</sub>) in the catalyst by the successive heat-treatment thereof, and the polysulfide is diluted in a pertinent organic solvent and then applied to the catalyst for impregnation. Since the said polysulfide is highly viscous, the viscosity would still be high even though it is diluted with an organic solvent and, as a result, there would be a problem that the polysulfide would hardly be penetrated into the inside of fine pores of the catalyst.

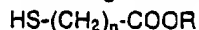
The catalyst to be treated by presulfurization is prepared by a method where an aluminium hydrate obtained from a starting material of sodium aluminate is shaped, dried and fired to give a  $\gamma$ -alumina, and the resulting  $\gamma$ -alumina is impregnated with an aqueous solution of a water-soluble compound of an active metal and then dried and heat-treated so that the active metal is converted into the corresponding oxide form, or by a method where an aluminium hydrate is blended with an aqueous solution of a water-soluble compound of an active metal and then shaped, dried and fired so that the active metal is carried on a carrier composed of the resulting  $\gamma$ -alumina in the form of the oxide form of the active metal.

## SUMMARY OF THE INVENTION

The object of the present invention is to provide catalysts for hydrotreating of hydrocarbons, which can be prepared more simply and more inexpensively than the above-mentioned conventional methods, which can be employed in hydrotreatment without pre-sulfurization and which can directly be applied to hydrotreatment without heat treatment, as well as to provide methods for preparing such catalysts.

The present inventors earnestly studied so as to overcome the above-mentioned problems and to achieve the above-mentioned object and, as a result, have found that the object may be attained by employing a water-soluble compound of a metal of Group VI and Group VIII of the Periodic Table as the active ingredient together with employment of an organic compound having one or two sulfurs in place of polysulfides and further employing phosphoric acid, and have hereby achieved the present invention.

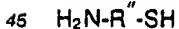
Specifically, the subject matter of the present invention is to provide a catalyst for hydrotreating of hydrocarbons, which is composed of a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium, at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table and at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:



where n represents an integer of from 1 to 3; and R represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, thio-acids of a general formula:



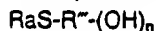
where R' represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, amino-substituted mercaptans of a general formula:



where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, dimercaptans of a general formula:



where R''' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, and mercapto-alcohols of a general formula:



where R'''' represents a hydrocarbon group having from 1 to 15 carbon atoms; Ra represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and n represents an integer of from 1 to 2.

In accordance with the first embodiment of the present invention, the catalyst of the present invention is prepared by a method where a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with a solution containing at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table and at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:

HS-(CH<sub>2</sub>)<sub>n</sub>-COOR,

thio-acids of a general formula:

R'-COSH,

amino-substituted mercaptans of a general formula:

5 H<sub>2</sub>N-R''-SH,

dimercaptans of a general formula:

HS-R''-SH, and

mercapto-alcohols of a general formula:

RaS-R''-(OH)<sub>n</sub>,

10 and the resulting blend is shaped and dried to prepare the said catalyst. (In the said formulae, n, R, R', R'' and R''' have the same meanings as mentioned above, and the same shall apply hereunder.)

In accordance with the second embodiment of the present invention, the catalyst of the present invention is prepared by a method where a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with an aqueous solution of at least one  
15 selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table, the resulting blend is shaped and then temporarily dried, and the thus dried shaped body is impregnated with a solution of at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:

HS-(CH<sub>2</sub>)<sub>n</sub>-COOR,

20 thio-acids of a general formula:

R'-COSH,

amino-substituted mercaptans of a general formula:

H<sub>2</sub>N-R''-SH,

dimercaptans of a general formula:

25 HS-R''-SH, and

mercapto-alcohols of a general formula:

RaS-R''-(OH)<sub>n</sub>,

and then again dried to prepare the said catalyst.

In accordance with the third object of the present invention, the catalyst of the present invention  
30 prepared by a method where a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with an aqueous solution of at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:

HS-(CH<sub>2</sub>)<sub>n</sub>-COOR,

thio-acids of a general formula:

35 R'-COSH,

amino-substituted mercaptans of a general formula:

H<sub>2</sub>N-R''-SH,

dimercaptans of a general formula:

HS-R''-SH, and

40 mercapto-alcohols of a general formula:

RaS-R''-(OH)<sub>n</sub>,

the resulting blend is shaped and then temporarily dried, and the thus dried shaped body is impregnated with an aqueous solution of at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table, and then again dried to prepare the said catalyst.

45 In accordance with the fourth embodiment of the present invention, there is provided a catalyst for hydrotreating hydrocarbons, which comprises a shaped body of a mixture composed of a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium, at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table, a phosphoric acid, and at least one organic compound selected from the group consisting of mercapto-carboxylic acids  
50 of a general formula:

HS-(CH<sub>2</sub>)<sub>n</sub>-COOR,

thio-acids of a general formula:

R'-COSH,

amino-substituted mercaptans of a general formula:

55 H<sub>2</sub>N-R''-SH,

dimercaptans of a general formula:

HS-R''-SH, and

mercapto-alcohols of a general formula:

$\text{RaS-R}''\text{-(OH)}_n$ .

In accordance with the fifth embodiment of the present invention, the catalyst of the fourth embodiment of the present invention is prepared by a method where a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with a solution containing at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table, phosphoric acid and at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:

$\text{HS-(CH}_2)_n\text{-COOR}$ ,

thio-acids of a general formula:

$\text{R}'\text{-COSH}$ ,

amino-substituted mercaptans of a general formula:

$\text{H}_2\text{N-R}''\text{-SH}$ ,

dimercaptans of a general formula:

$\text{HS-R}''\text{-SH}$ , and

mercapto-alcohols of a general formula:

$\text{RaS-R}''\text{-(OH)}_n$ ,

and the resulting blend is shaped and dried to prepare the said catalyst of the fourth embodiment of the present invention.

In accordance with the sixth embodiment of the present invention, the catalyst of the fourth embodiment of the present invention is prepared by a method where a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with an aqueous solution comprising at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table and phosphoric acid, the resulting blend is shaped and then temporarily dried, and the thus dried shaped body is impregnated with a solution of at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:

$\text{HS-(CH}_2)_n\text{-COOR}$ ,

thio-acids of a general formula:

$\text{R}'\text{-COSH}$ ,

amino-substituted mercaptans of a general formula:

$\text{H}_2\text{N-R}''\text{-SH}$ ,

dimercaptans of a general formula:

$\text{HS-R}''\text{-SH}$ , and

mercapto-alcohols of a general formula:

$\text{RaS-R}''\text{-(OH)}_n$ .

and then again dried to prepare the said catalyst of the fourth embodiment of the present invention.

In accordance with the seventh embodiment of the present invention, the catalyst of the fourth embodiment of the present invention is prepared by a method where a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with a solution comprising at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table and at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:

$\text{HS-(CH}_2)_n\text{-COOR}$ ,

thio-acids of a general formula;

$\text{R}'\text{-COSH}$ ,

amino-substituted mercaptans of a general formula:

$\text{H}_2\text{N-R}''\text{-SH}$ ,

dimercaptans of a general formula:

$\text{HS-R}''\text{-SH}$ , and

mercapto-alcohols of a general formula:

$\text{RaS-R}''\text{-(OH)}_n$ ,

the resulting blend is shaped and then temporarily dried, and the thus dried shaped body is impregnated with an aqueous solution of phosphoric acid and then again dried to prepare the said catalyst of the fourth embodiment of the present invention.

In accordance with the eighth embodiment of the present invention, the catalyst of the fourth embodiment of the present invention is prepared by a method where a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with a solution containing phosphoric acid and at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:

HS-(CH<sub>2</sub>)<sub>n</sub>-COOR,

thio-acids of a general formula:

R'-COSH,

amino-substituted mercaptans of a general formula:

5 H<sub>2</sub>N-R''-SH,

dimercaptans of a general formula:

HS-R''-SH, and

mercapto-alcohols of a general formula:

RaS-R''-(OH)<sub>n</sub>,

10 the resulting blend is shaped and then temporarily dried, and the thus dried shaped body is impregnated with an aqueous solution of at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table and then again dried to prepare the said catalyst of fourth embodiment of the present invention.

In accordance with the ninth embodiment of the present invention, the catalyst of the fourth embodi-  
15 ment of the present invention is prepared by a method where a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with an aqueous solution of at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table, the resulting blend is shaped and then temporarily dried, and the thus dried shaped body is impregnated with a solution containing phosphoric acid and at least one organic compound selected from  
20 the group consisting of mercapto-carboxylic acids of a general formula:

HS-(CH<sub>2</sub>)<sub>n</sub>-COOR,

thio-acids of a general formula:

R'-COSH,

amino-substituted mercaptans of a general formula:

25 H<sub>2</sub>N-R''-SH,

dimercaptans of a general formula:

HS-R''-SH, and

mercapto-alcohols of a general formula:

RaS-R''-(OH)<sub>n</sub>,

30 and then again dried to prepare the said catalyst of the fourth embodiment of the present invention.

In accordance with the tenth embodiment of the present invention, the catalyst of the fourth embodi-  
ment of the present invention is prepared by a method where a carrier substance consisting essentially of  
an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with a solution of at  
least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general  
35 formula:

HS-(CH<sub>2</sub>)<sub>n</sub>-COOR,

thio-acids of a general formula:

R'-COSH,

amino-substituted mercaptans of a general formula:

40 H<sub>2</sub>N-R''-SH,

dimercaptans of a general formula:

HS-R''-SH, and

mercapto-alcohols of a general formula:

RaS-R''-(OH)<sub>n</sub>,

45 the resulting blend is shaped and then temporarily dried, and the thus dried shaped body is impregnated with an aqueous solution containing at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table and phosphoric acid, and then again dried to prepare the said catalyst of the fourth embodiment of the present invention.

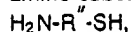
In accordance with the eleventh embodiment of the present invention, the catalyst of the fourth  
50 embodiment of the present invention is prepared by a method where a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with an aqueous solution of phosphoric acid, the resulting blend is shaped and then temporarily dried, and the thus dried shaped body is impregnated with a solution containing at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table and at least one organic compound  
55 selected from the group consisting of mercapto-carboxylic acids of a general formula:

HS-(CH<sub>2</sub>)<sub>n</sub>-COOR,

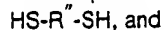
thio-acids of a general formula:

R'-COSH,

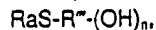
amino-substituted mercaptans of a general formula:



dimercaptans of a general formula:



5 mercapto-alcohols of a general formula:



and then again dried to prepare the said catalyst of the fourth embodiment of the present invention.

## 10 DETAILED DESCRIPTION OF THE INVENTION

As the carrier substance for use in the present invention, which consists essentially of an oxide of aluminium and/or an oxide hydrate of aluminium, a  $\gamma$ -alumina or boehmite obtainable by heat-treating a  
 15 hydrate of aluminium is employed. Boehmite has a structural formula of  $\text{AlO}(\text{OH})$  (or a chemical formula of  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  as monohydrate of alumina), which is an aluminium oxide hydrate. Sodium aluminate is hydrolyzed to give a gel substance, and this is dehydrated by filter-pressing to prepare a dehydrated boehmite gel (hereinafter referred to as "dehydrated boehmite"); or the dehydrated boehmite is spray-dried (hereinafter referred to as "spray-dried boehmite"). These dehydrated boehmite and spray-dried boehmite  
 20 can be employed in the present invention. Boehmite is also prepared as a natural boehmite ore, which contains impurities of  $\text{SiO}_2$ ,  $\text{FeO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ , etc. When heated, boehmite is dehydrated to  $\gamma$ -alumina, to  $\delta$ -alumina and to  $\theta$ -alumina in order, and this finally becomes  $\alpha$ -alumina (corundum) at 1100 to 1200 °C. Accordingly, as boehmite is an intermediate between aluminium hydroxide and aluminium oxide, it may be employed singly or may also be employed in combination with an active  $\gamma$ -alumina. Alternatively,  
 25 only  $\gamma$ -alumina may also be employed as the carrier substance. In addition, silica or titania may be blended with the said compound and the resulting mixture may also be used as the carrier substance.

As the water-soluble compounds of metals of Group VI of the Periodic Table for use in the present invention, molybdenum (Mo) and tungsten (W) which are generally employed as active metals of catalysts are preferably employed as ammonium molybdate and ammonium tungstate respectively. Where molybdenum trioxide and tungsten trioxide are employed, ammonia gas is applied thereto and they are used in  
 30 the form of ammonium molybdate and ammonium tungstate. As the water-soluble compounds of metals of Group VIII of the Periodic Table for use in the present invention, cobalt (Co) and nickel (Ni) which are generally employed as active metals of catalysts are preferably employed as cobalt nitrate, cobalt carbonate, nickel nitrate and nickel carbonate. They are used singly or in combination, in the form of an aqueous solution. Where the water-soluble compounds of the said active metals are heated together with at least one of mercapto-carboxylic acids of a general formula  $\text{HS}-(\text{CH}_2)_n-\text{COOR}$ , thio-acids of a general formula  $\text{R}'-\text{COSH}$ , amino-substituted mercaptans of a general formula  $\text{H}_2\text{N}-\text{R}''-\text{SH}$ , dimercaptans of a general formula  $\text{HS}-\text{R}''-\text{SH}$  and mercapto-alcohols of a general formula  $\text{RaS}-\text{R}''-(\text{OH})_n$  (hereinafter referred to "mercapto-carboxylic acids and other sulfurizing agents"), they form sulfides such as  $\text{MoS}_2$ ,  $\text{WS}_2$ ,  $\text{CoS}$ ,  $\text{NiS}$   
 40 and the like which are highly active in hydrogenation reaction.

In the mercapto-carboxylic acids and other sulfurizing agents for use in the present invention, the portion which is functional to sulfurization of active metals comprises one or two sulfur components in the molecule of the respective sulfurizing agent compounds. Accordingly, where the number of the carbon atoms in the hydrocarbon group in the molecule of the said sulfurizing agent compound is large, the portion  
 45 which is functional as the sulfurizing agent in the molecule would thereby be relatively small and, as a result, not only the compound is uneconomical but also the compound would unfavorably bring superfluous carbons and hydrogens into the catalyst. Because of such reason, the sulfurizing compounds to be employed in the present invention are preferred to have carbon atoms as few as possible. Specifically, the number of the carbon atoms in the compounds is preferably at most up to 15. More precisely, as the mercapto-carboxylic acids of a general formula  $\text{HS}-(\text{CH}_2)_n-\text{COOR}$  (where n represents an integer of from 1 to 3; and R represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms), for example, mercapto-acetic acid ( $\text{HSCH}_2\text{COOH}$ ),  $\beta$ -mercapto-propionic acid ( $\text{HSCH}_2\text{CH}_2\text{COOH}$ ) or the like mercapto-carboxylic acids as well as alkali metal salts, alkaline earth metal salts and ammonium salts thereof can be employed. In particular, metal ion-free  
 50 acid type and ammonium salt type compounds which do not form any substance to be a catalyst poison to hydrogenation reaction are preferred. These can be used also together with phosphoric acid in the form of a phosphoric acid-containing acidic aqueous solution. In addition, there are also mentioned mercapto-carboxylic acid esters such as methyl mercapto-acetate ( $\text{HSCH}_2\text{COOCH}_3$ ), ethyl 2-mercapto-acetate

(HSCH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub>), 2-ethylhexyl mercapto-acetate (HSCH<sub>2</sub>COOC<sub>8</sub>H<sub>17</sub>) or methyl 3-mercapto-propionate (HSCH<sub>2</sub>CH<sub>2</sub>COOCH<sub>3</sub>). As the thio-acids of a general formula R'-COSH (where R' represents a hydrocarbon group having from 1 to 15 carbon atoms), there are mentioned, for example, thio-acetic acid (CH<sub>3</sub>COSH) and thio-benzoic acid (C<sub>6</sub>H<sub>5</sub>COSH). As the amino-substituted mercaptans of a general formula H<sub>2</sub>N-R''-SH (where R'' represents a divalent hydrocarbon group), for example, there are mentioned 2-aminoethane-thiol (H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>SH) and 4-aminothiophenol (H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SH). As the dimercaptans of a general formula HS-R''-SH (where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, for example, there are mentioned ethanedithiol (HSCH<sub>2</sub>CH<sub>2</sub>SH) and 1,4-butanedithiol (HS(CH<sub>2</sub>)<sub>4</sub>SH). As the mercapto-alcohols of a general formula RaS-R'''-(OH)<sub>n</sub> (where R''' represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group; Ra represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and n represents an integer of from 1 to 2), for example, there are mentioned 2-mercaptoethanol (HSCH<sub>2</sub>CH<sub>2</sub>OH), 2-(methylthio)ethanol (CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>OH), 2-(ethylthio)ethanol (C<sub>2</sub>H<sub>5</sub>SCH<sub>2</sub>CH<sub>2</sub>OH), 3-mercapto-2-butanol (CH<sub>3</sub>CH(SH)CH(OH)CH<sub>3</sub>), 4-mercaptophenol (HSC<sub>6</sub>H<sub>4</sub>OH), 2-(methylthio)phenol (CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>OH), 4-(methylthio)phenol (CH<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>OH), 2-(ethylthio)phenol (C<sub>2</sub>H<sub>5</sub>SC<sub>6</sub>H<sub>4</sub>OH), 3-mercapto-1,2-propanediol (HSCH<sub>2</sub>CH<sub>2</sub>(OH)CH<sub>2</sub>OH), 3-methylthio-1,2-propanediol (CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>(OH)CH<sub>2</sub>OH) and 3-ethylthio-1,2-propanediol (C<sub>2</sub>H<sub>5</sub>SCH(OH)CH<sub>2</sub>OH). The said examples of the compounds are preferably employed in the present invention but do not whatsoever restrict the scope of the present invention.

Regarding the content of the metals of Group VI and Group VIII of the Periodic Table in the catalyst as the active metal component therein, where the catalyst contains only one kind of the said active metals, the content of the metal in the catalyst is preferred to fall within the scope of from 1 to 30 % by weight as the oxide of the active metal. On the other hand, where the catalyst contains both the metal of Group VI and the metal of Group VIII in combination, it is preferred that the content of the metal of Group VI is from 5 to 30 % by weight and that of the metal of Group VIII is from 1 to 8 % by weight, both as the oxides of the said metals.

The amount of the mercapto-carboxylic acids and other sulfurizing agents to be used in accordance with the present invention is preferably from 1 to 3 equivalents to the sulfur amount necessary for forming sulfides, which are highly active in hydrogenation reaction, such as MoS<sub>2</sub>, WS<sub>2</sub>, CoS or NiS, from the metals of Group VI and Group VIII of the Periodic Table. If the amount is less than one equivalent, the activity could not be attained sufficiently. On the other hand, if it is more than three equivalents, the activity would be no more augmented. Accordingly, the amount falling within the said range is proper.

Phosphoric acid may be incorporated into the catalyst in an amount of about 3 % by weight or so as P<sub>2</sub>O<sub>5</sub>.

The catalyst of the present invention can be prepared from the above-mentioned raw materials in the proportion as mentioned above, in accordance with the methods mentioned below. As the first method, the carrier substance, the active metal and the sulfurizing agent are kneaded, shaped and dried (Method I). As the second method, the carrier substance and the active metal are blended, shaped and dried, and the dried shaped body is impregnated with the sulfurizing agent solution and re-dried (Method II). As the third method, the carrier substance and the sulfurizing agent are kneaded, shaped and dried, and the dried shaped body is impregnated with the active metal solution and re-dried (Method III). As the fourth method, the carrier substance, the active metal, phosphoric acid and the sulfurizing agent are kneaded, shaped and dried (Method IV). As the fifth method, the carrier substance, the active metal and phosphoric acid are kneaded, shaped and dried, and the dried shaped body is impregnated with the sulfurizing agent solution and re-dried (Method V). As the sixth method, the carrier substance, the active metal and the sulfurizing agent are kneaded, shaped and dried, and the dried shaped body is impregnated with phosphoric acid solution and re-dried (Method VI). As the seventh method, the carrier substance, phosphoric acid and the sulfurizing agent are kneaded, shaped and dried, the dried shaped body is impregnated with the active metal solution and re-dried (Method VII). As the eighth method, the carrier substance and the active metal are kneaded, shaped and dried, and the dried shaped body is impregnated with a solution containing phosphoric acid and the sulfurizing agent and then re-dried (Method VIII). As the ninth method, the carrier substance and the sulfurizing agent are kneaded, shaped and dried, and the dried shaped body is impregnated with a solution containing the active metal and phosphoric acid and then re-dried (Method IX). As the tenth method, the carrier substance and phosphoric acid are kneaded, shaped and dried, and the dried shaped body is impregnated with a solution containing the active metal and the sulfurizing agent and then re-dried (Method X).

As the solvent for dissolving the water-soluble compounds and sulfides of the active metals, water is most economically employed.

The drying temperature in the said methods preferably falls within the scope of from 50 to 200 °C; and the drying time therein preferably falls within the scope of from 2 to 20 hours.



For practical use of the catalysts as prepared by the methods of the present invention, the freshly dried catalyst may be filled in a reactor column and can be utilized for hydrotreating a hydrocarbon oil in the column. The water content in the catalyst as introduced therein in the course of the step of preparing the catalyst may be dried and removed therefrom after the catalyst has been put in the reactor column.

5 Since the catalyst of the present invention contains the mercapto-carboxylic acid and other sulfurizing agent in the form as carried on the carrier substance together with the water-soluble compound of the active metal, the active metal can be converted into the sulfide thereof in the course of the step of elevating the temperature of the reaction system up to the reaction temperature for dehydration and desulfurization of the hydrocarbon oil to be processed with the catalyst and, as a result, the catalyst can directly be utilized in the hydrodesulfurization for the hydrocarbon oil without presulfurization of the catalyst.

10 In addition, the catalysts of the present invention have a higher activity than the conventional catalysts which require presulfurization. Although not clarified as yet, the reason is considered that the mercapto-carboxylic acids and other sulfurizing agents would form a soluble coordination compound (metal mercaptide) together with the water-soluble compounds of the active metals and the resulting soluble coordinate compound would be carried on the carrier substance in a highly dispersed form.

15 The following examples are intended to illustrate the present invention in more detail but not to limit it in any way.

In the following examples, all the catalysts were shaped by extrusion moulting into a cylindrical shape having a diameter of 1.6 mm and a length of from 3 to 5 mm.

20 The catalyst activity was evaluated on the basis of hydrodesulfurization of Kuwait straight-run light gas oil (KSRLGO).

The KSRLGO used in the reaction had the following property.

25	Specific Gravity (15/4 °C)	0.844
	Sulfur Content (% by weight)	1.13
	Nitrogen Content (ppm by weight)	162
	Distillation Characteristic:	
30	Initial Boiling point (°C)	203.3
	50 vol.% Point (°C)	299.0
	End Point (°C)	391.8

35 The reaction was effected by the use of a flow method reaction device, under the following reaction conditions.

40	Amount of Catalyst	3 ml
	Liquid Hourly Space Velocity of Raw Material Oil	2.0 hr <sup>-1</sup>
	Reaction Pressure (hydrogen pressure)	30 kg/cm <sup>2</sup>
	Reaction Temperature	330 °C
	Hydrogen/Oil Ratio	300 N-liter/liter
45	Oil-Introducing Time	8 hr

The oil being processed was sampled every two hours, and the sulfur content in the oil and the desulfurization percentage were obtained. The desulfurization percentage as mentioned in the following examples indicates an average of the values of the desulfurization percentage as obtained from the sulfur content in the processed oil as sampled four hours, six hours and eight hours after the start of the reaction.

#### EXAMPLE 1: (Method-I)

55 211.1 g of 50 wt.% ammonium thioglycolate was added to 300 ml of a solution prepared from 37.0 g of molybdenum trioxide, 15.8 g of cobalt carbonate (Co content: 49.1 wt.%), ammonia gas and water to obtain a metal mercaptide solution (pH 7.0).

The metal mercaptide solution and 272 g of spray-dried boehmite powder (Al<sub>2</sub>O<sub>3</sub>: 73.5 wt.%) were put

in a kneader and kneaded to obtain a blend, which was then shaped.

The shaped body was dried at 100° C for 16 hours to prepare a catalyst (Catalyst-1).

The breaking strength of the Catalyst-1 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-1, molybdenum content was 15 % by weight as MoO<sub>3</sub>, and cobalt content was 4 % by weight as CoO. The amount of ammonium thioglycolate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-1 was 84.1 %.

10

#### EXAMPLE 2: (Method I)

147.4 g of 50 wt.% ammonium thioglycolate solution was added to 300 ml of a solution prepared from 37.0 g of tungsten trioxide, 15.8 g of cobalt carbonate (Co content: 49.1 wt.%), ammonia gas and water to obtain a metal mercaptide solution (pH 7.5).

The metal mercaptide solution and 272 g of the same spray-dried boehmite powder as that used in Example 1 were put in a kneader and kneaded to obtain a blend, which was then shaped.

The shaped body was dried at 100° C for 16 hours to prepare a catalyst (Catalyst-2).

The breaking strength of the Catalyst-2 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-2, tungsten content was 15 % by weight as WO<sub>3</sub>, and cobalt content was 4 % by weight as CoO. The amount of ammonium thioglycolate used was 1.5 times of the theoretical amount of sulfur necessary to convert W and Co into WS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-2 was 83.0 %

25

#### EXAMPLE 3: (Method II)

400 ml of an aqueous solution (pH 8.0) was prepared from 37.0 g of molybdenum trioxide, 15.8 g of cobalt carbonate (Co content: 49.1 wt.%), ammonia gas and water.

The solution and 272 g of the same spray-dried boehmite powder as that used in Example 1 were put in a kneader and kneaded to obtain a blend, which was then shaped.

The shaped body was dried for 16 hours at 100° C. Next, the dried body was impregnated with 120 ml of an aqueous solution containing 109.1 g of mercapto-acetic acid and then dried for 16 hours at 100° C. Accordingly, Catalyst-3 was prepared.

The breaking strength of the Catalyst-3 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-3, molybdenum content was 15 % by weight as MoO<sub>3</sub> and cobalt content was 4 % by weight as CoO. The amount of mercapto-acetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-3 was 82.9 %.

40

#### EXAMPLE 4: (Method III)

272 g of the same spray-dried boehmite powder as that used in Example 1 and 300 ml of an aqueous solution containing 211.1 g of 50 wt.% ammonium thioglycolate were put in a kneader and kneaded to obtain a blend, which was then shaped.

The shaped body was dried at 100° C for 16 hours. The dried shaped body was then completely dipped in 150 ml of a solution prepared from 37.0 g of molybdenum trioxide, 15.8 g of cobalt carbonate (Co content: 49.1 wt.%), ammonia gas and water (pH 7.5) and thereafter dried at 100° C for 16 hours. The said operation was repeated twice, and accordingly Catalyst-4 was prepared.

The breaking strength of the Catalyst-4 was 1.5 kg/mm or more.

Regarding the active metal content of the Catalyst-4, molybdenum content was 15 % by weight as MoN<sub>3</sub> and cobalt content was 4 % by weight as CoO. The amount of ammonium thioglycolate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-4 was 83.6 %.

55

#### EXAMPLES 5, 6 AND 7: (Method IV)

72.7 g of mercapto-acetic acid was added to 300 ml of a solution prepared from 38.5 g of molybdenum trioxide, 16.4 g of cobalt carbonate (Co content: 49.1 wt.%), 12.5 g of 85 wt.% phosphoric acid and water to obtain a phosphoric acid-containing metal mercaptide solution (pH 0.6).

The metal mercaptide solution and 673 g of dehydrated boehmite ( $\text{Al}_2\text{O}_3$ : 29.7 wt.%) were put in a heating kneader and kneaded with heating at 95 °C so as to evaporate the excess water, to obtain a blend, which was then shaped.

The shaped body was dried at 100 °C for 16 hours to obtain a catalyst (Catalyst-5).

Catalyst-6 and Catalyst-7 were prepared in the same manner as above, except that mercapto-acetic acid was used in an amount of 109.1 g and 145.5 g, respectively.

The breaking strength of the Catalysts 5, 6 and 7 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalysts 5, 6 and 7, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content is 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of mercapto-acetic acid used was 1.0 time, 1.5 times and 2.0 times, respectively, of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with each of the Catalysts 5, 6 and 7 was 82.5 %, 83.5 % and 82.0 %, respectively.

#### EXAMPLE 8: (Method IV)

109.1 g of mercapto-acetic acid was added to 300ml of a solution prepared from 38.5 g of molybdenum trioxide, 16.4 g of cobalt carbonate (Co content: 49.1 wt.%), 12.5 g of 85 wt.% phosphoric acid and water, to obtain a phosphoric acid-containing metal mercaptide solution (pH 0.6).

The metal mercaptide solution and 272 g of the same spray-dried boehmite powder as that used in Example 1 were put in a kneader and kneaded to obtain a blend, which was then shaped.

The shaped body was dried at 100 °C for 16 hours to prepare a catalyst (Catalyst-8).

The breaking strength of the Catalyst-8 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-8, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of mercapto-acetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-8 was 8.18 %.

#### EXAMPLE 9: (Method IV)

109.1 g of mercapto-acetic acid was added to 300 ml of a solution prepared from 38.5 g of molybdenum trioxide, 16.4 g of cobalt carbonate (Co content: 49.1 wt.%), 12.5 g of 85 wt.% phosphoric acid and water, to obtain a phosphoric acid-containing metal mercaptide solution (pH 0.6).

The metal mercaptide solution and 200 g of  $\gamma$ -alumina powder were put in a kneader and kneaded to obtain a blend comprising the said  $\gamma$ -alumina and metal mercaptide. This was thereafter shaped.

The shaped body was dried at 100 °C for 16 hours to prepare a catalyst (Catalyst-9).

The breaking strength of the Catalyst-9 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-9, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of mercapto-acetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-9 was 81.5 %.

#### EXAMPLE 10: (Method IV)

106.8 g of mercapto-propionic acid was added to 300 ml of a solution prepared from 38.5 g of molybdenum trioxide, 16.4 g of cobalt carbonate (Co content: 49.1 wt.%), 12.5 g of 85 wt.% phosphoric acid and water, to obtain a phosphoric acid-containing metal mercaptide solution (pH 0.7).

The metal mercaptide solution and 673 g of the same dehydrated boehmite as that used in Examples 5, 6 and 7 were put in a heating kneader and kneaded with heating at 95 °C so as to evaporate the excess water therefrom, to obtain a blend, which was then shaped.

The shaped body was dried at 100 ° C for 16 hours to prepare a catalyst (Catalyst-10).

The breaking strength of the Catalyst-10 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-10, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of mercapto-propionic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-10 was 86.0 %.

#### 10 EXAMPLE 11: (Method IV)

219.6 g of 50 wt.% ammonium thioglycolate solution was added to 300 ml of a solution prepared from 38.5 g of molybdenum trioxide, 16.4 g of cobalt carbonate (Co content: 49.1 wt.%), 12.5 g of 85 wt.% phosphoric acid and water, to obtain a phosphoric acid-containing metal mercaptide solution (pH 5.2).

15 The metal mercaptide solution and 673 g of the same dehydrated boehmite as that used in Examples 5, 6 and 7 were put in a heating kneader and kneaded with heating at 95 ° C so as to evaporate the excess water therefrom, to obtain a blend, which was then shaped.

The shaped body was dried at 100 ° C for 16 hours to prepare a catalyst (Catalyst-11).

The breaking strength of the Catalyst-11 was 1.5 kg/mm or more.

20 Regarding the active metal content in the Catalyst-11, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of ammonium thioglycolate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-11 was 83.4 %.

25

#### EXAMPLE 12: (Method IV)

154.8 g of mercapto-acetic acid was added to 300 ml of a solution prepared from 57.6 g of molybdenum trioxide, 20.9 g of nickel carbonate (Ni content: 43.3 wt.%), 30.4 g of 85 wt.% phosphoric acid and water, to obtain a phosphoric acid-containing metal mercaptide solution (pH 0.2).

The metal mercaptide solution and 272 g of the same spray-dried boehmite powder as that used in Example 1 were put in a kneader and kneaded to obtain a blend, which was then shaped.

The shaped body was dried at 100 ° C for 16 hours to prepare a catalyst (Catalyst-12).

35 The breaking strength of the Catalyst-12 was 1.5 kg/mm or more.

Regarding the active metal content of the Catalyst-12, molybdenum content was 15 % by weight as MoO<sub>3</sub>, nickel content was 4 % by weight as NiO and phosphorus content was 6.5 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of mercapto-acetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Ni into MoS<sub>2</sub> and NiS, respectively.

40 The desulfurization percentage with the catalyst was 84.2 %.

#### EXAMPLE 13: (Method V)

45 400 ml of an aqueous solution (pH 2.0) was prepared from 38.5 g of molybdenum trioxide, 16.4 g of cobalt carbonate (Co content: 49.1 wt.%), 12.5 g of 85 wt.% phosphoric acid and water.

The solution and 272 g of the same spray-dried boehmite powder as that used in Example 1 were put in a kneader and kneaded to obtain a blend, which was then shaped.

50 The shaped body was dried at 100 ° C for 16 hours. Next, the dried body was completely impregnated with 150 ml of an aqueous solution containing 109.1 g of mercapto-acetic acid and then again dried at 100 ° C for 16 hours. Accordingly, Catalyst-13 was prepared.

The breaking strength of the Catalyst-13 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-13, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content is 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of mercapto-acetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-13 was 77.8 %.

EXAMPLE 14: (Method VI)

219.6 g of 50 wt.% ammonium thioglycolate was added to a solution prepared from 38.5 g of molybdenum trioxide, 16.4 g of cobalt carbonate (Co content: 49.1 wt.%), ammonia gas and water, to obtain  
 5 300 ml of a metal mercaptide solution (pH 7.0).

The metal mercaptide solution and 272 g of the same spray-dried boehmite powder as that used in Example 1 were put in a kneader and kneaded to obtain a blend, which was then shaped.

The shaped body was dried at 100 °C for 16 hours. Next, the dried body was completely impregnated with 50 ml of an aqueous solution containing 12.5 g of 85 wt.% phosphoric acid and then again dried at  
 10 100 °C for 16 hours. Accordingly, Catalyst-14 was prepared.

The breaking strength of the Catalyst-14 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-14, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of ammonium thioglycolate used was 1.5 times of the theoretical amount of sulfur necessary to  
 15 convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-14 was 82.8 %.

EXAMPLE 15: (Method VII)

272 g of the same spray-dried boehmite as that used in Example 1 and 300 ml of an aqueous solution containing 109.1 g of mercapto-acetic acid and 12.5 g of 85 wt.% phosphoric acid were put in a kneader and kneaded, and the resulting blend was shaped.

The shaped body was dried at 100 °C for 16 hours.

25 The dried body was completely impregnated with 150 ml of a solution (pH 7.5) prepared from 38.5 g of molybdenum trioxide, 16.4 g of cobalt carbonate (Co content: 49.1 wt.%), ammonia gas and water and then again dried at 100 °C for 16 hours. Accordingly, Catalyst-15 was prepared.

The breaking strength of the Catalyst-15 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-15, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of mercapto-acetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert  
 30 Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-15 was 83.5 %.

EXAMPLE 16: (Method VIII)

300 ml of a solution (pH 7.0) prepared from 38.5 g of molybdenum trioxide, 16.4 g of cobalt carbonate (Co content: 49.1 wt.%), ammonia gas and water and 272 g of the same spray-dried boehmite powder as that used in Example 1 were put in a kneader and kneaded to obtain a blend, which was then shaped.

The shaped body was dried at 100 °C for 16 hours. Next, the dried body was completely impregnated with 200 ml of an aqueous solution containing 12.5 g of 85 wt.% phosphoric acid and 109.1 g of mercapto-acetic acid and then again dried at 100 °C for 16 hours. Accordingly, Catalyst-16 was prepared.

The breaking strength of the Catalyst-16 was 1.5 kg/mm or more.

45 Regarding the active metal content in the Catalyst-16, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of mercapto-acetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-16 was 83.2 %.

EXAMPLE 17: (Method IX)

272 g of the same spray-dried boehmite powder as that used in Example 1 and 300 ml of an aqueous solution containing 109.1 g of mercapto-acetic acid were put in a kneader and kneaded, and the resulting blend was shaped. The shaped body was dried at 100 °C for 16 hours.

The dried shaped body was completely impregnated with 100 ml of a solution (pH 2.0) prepared from 38.5 g of molybdenum trioxide, 16.4 g of cobalt carbonate (Co content: 49.1 wt.%), 12.5 g of 85 wt.%

phosphoric acid and water and then again dried at 100° C for 16 hours. Accordingly, Catalyst-17 was prepared.

The breaking strength of the Catalyst-17 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-17, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of mercapto-acetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-17 was 84.2 %.

10

#### EXAMPLE 18: (Method X)

272 g of the same spray-dried boehmite powder as that used in Example 1 and 300 ml of an aqueous solution containing 12.5 g of 85 wt.% phosphoric acid were put in a kneader and kneaded, and the resulting blend was shaped.

The shaped body was dried at 100° C for 16 hours.

The dried shaped body was completely impregnated with 250 ml of a solution (pH 6.2) of a metal mercaptide obtained by adding 219.6 g of ammonium thioglycolate to a solution prepared from 38.5 g of molybdenum trioxide, 16.4 g of cobalt carbonate (Co content: 49.1 wt.%), ammonia gas and water, and then again dried at 100° C for 16 hours. Accordingly, Catalyst-18 was prepared.

The breaking strength of the Catalyst-18 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-18, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of ammonium thioglycolate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-18 was 83.0 %.

#### Example 19: (Method I)

Catalyst-19 was prepared in the same manner as Example 1, except that 102.7 g of methyl mercaptoacetate was used as the sulfurizing agent.

The breaking strength of the Catalyst-19 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-19, molybdenum content was 15 % by weight as MoO<sub>3</sub> and cobalt content was 4 % by weight as CoO. The amount of methyl mercapto-acetate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-19 was 82.7 %.

40

#### Example 20: (Method-I)

Catalyst-20 was prepared in the same manner as Example 2, except that 71.7 g of methyl mercaptoacetate was used as the sulfurizing agent.

The breaking strength of the Catalyst-20 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-20, tungsten content was 15 % by weight as WO<sub>3</sub> and cobalt content was 4 % by weight as CoO. The amount of methyl mercapto-acetate used was 1.5 times of the theoretical amount of sulfur necessary to convert W and Co into WS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-20 was 82.1 %.

50

#### EXAMPLE 21: (Method II)

Catalyst-21 was prepared in the same manner as Example 3, except that 116.3 g of methyl 3-mercapto-propionate was used as the sulfurizing agent.

The breaking strength of the Catalyst-21 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-21, molybdenum content was 15 % by weight as MoO<sub>3</sub> and cobalt content was 4 % by weight as CoO. The amount of methyl 3-mercapto-propionate used

was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-21 was 81.0 %.

5

EXAMPLE 22: (Method III)

Catalyst-22 was prepared in the same manner as Example 4, except that 116.3 g of ethyl 2-mercaptoacetate was used as the sulfurizing agent.

10 The breaking strength of the Catalyst-22 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-22, molybdenum content was 15 % by weight as  $\text{MoO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The amount of ethyl 2-mercaptoacetate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

15 The desulfurization percentage with the Catalyst-22 was 81.5 %.

EXAMPLE 23: (Method IV)

20 Catalyst-23 was obtained in the same manner as Example 5, except that 106.8 g of methyl mercaptoacetate was used as the sulfurizing agent.

The breaking strength of the Catalyst-23 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-23, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of methyl mercaptoacetate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

25 The desulfurization percentage with the Catalyst-23 was 82.2 %.

30 EXAMPLE 24: (Method IV)

Catalyst-24 was obtained in the same manner as Example 8, except that 106.8 g of methyl mercaptoacetate was used as the sulfurizing agent.

The breaking strength of the Catalyst-24 was 1.5 kg/mm or more.

35 Regarding the active metal content in the Catalyst-24, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of methyl mercaptoacetate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-24 was 83.0 %.

40

EXAMPLE 25: (Method IV)

45 Catalyst-25 was prepared in the same manner as Example 9, except that 120.9 g of methyl 3-mercapto-propionate was used as the sulfurizing agent.

The breaking strength of the Catalyst-25 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-25, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of methyl 3-mercapto-propionate used as 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

50 The desulfurization percentage with the Catalyst-25 was 82.0 %.

EXAMPLE 26: (Method IV)

55

Catalyst-26 was prepared in the same manner as Example 5, except that 120.9 g of methyl 3-mercapto-propionate was used as the sulfurizing agent.

The breaking strength of the Catalyst-26 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-26, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of methyl 3-mercapto-propionate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

5 The desulfurization percentage with the Catalyst-26 was 81.1 %.

#### EXAMPLE 27: (Method IV)

10 Catalyst-27 was prepared in the same manner as Example 8, except that 120.9 g of methyl 3-mercapto-propionate was used as the sulfurizing agent.

The breaking strength of the Catalyst-27 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-27, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of methyl 3-mercapto-propionate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-27 was 81.5 %.

#### 20 EXAMPLE 28: (Method IV)

Catalyst-28 was prepared in the same manner as Example 12, except that 151.6 g of methyl mercapto-acetate was used as the sulfurizing agent.

The breaking strength of the Catalyst-28 was 1.5 kg/mm or more.

25 Regarding the active metal content in the Catalyst-28, molybdenum content was 20 % by weight as  $\text{MoO}_3$ , nickel content was 4 % by weight as  $\text{NiO}$  and phosphorus content was 6.5 % by weight as  $\text{P}_2\text{O}_5$ . The amount of methyl mercapto-acetate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Ni into  $\text{MoS}_2$  and  $\text{NiS}$ , respectively.

The desulfurization percentage with the Catalyst-28 was 79.0 %.

30

#### EXAMPLE 29: (Method V)

35 Catalyst-29 was prepared in the same manner as Example 13, except that 106.8 g of methyl mercapto-acetate was used as the sulfurizing agent.

The breaking strength of the Catalyst-29 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-29, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of methyl mercapto-acetate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

40 The desulfurization percentage with the Catalyst-29 was 81.8 %.

#### EXAMPLE 30: (Method VI)

45

Catalyst-30 was prepared in the same manner as Example 14, except that 120.9 g of ethyl 2-mercapto-acetate was used as the sulfurizing agent.

The breaking strength of the Catalyst-30 was 1.5 kg/mm or more.

50 Regarding the active metal content in the Catalyst-30, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of ethyl 2-mercapto-acetate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-30 was 81.8 % by weight.

55

#### EXAMPLE 31: (Method VII)

Catalyst-31 was prepared in the same manner as Example 15, except that 205.5 g of 2-ethylhexyl



mercapto-acetat was used as the sulfurizing agent.

The breaking strength of the Catalyst-31 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-31, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 2-ethylhexyl mercapto-acetate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-31 was 81.2 %.

#### 10 EXAMPLE 32: (Method VIII)

Catalyst-32 was prepared in the same manner as Example 16, except that 120.9 g of methyl 3-mercapto-propionate was used as the sulfurizing agent.

The breaking strength of the Catalyst-32 was 1.5 kg/mm or more.

15 Regarding the active metal content in the Catalyst-32, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of methyl 3-mercapto-propionate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-32 was 81.2 %.

20

#### EXAMPLE 33: (Method IX)

25 Catalyst-33 was obtained in the same manner as Example 17, except that 106.8 g of methyl mercapto-acetate was used as the sulfurizing agent.

The breaking strength of the Catalyst-33 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-33, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of methyl mercapto-acetate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

30 The desulfurization percentage with the Catalyst-33 was 81.9 %.

#### EXAMPLE 34: (Method X)

35 Catalyst-34 was prepared in the same manner as Example 18, except that 120.9 g of methyl 3-mercapto-propionate was used as the sulfurizing agent.

The breaking strength of the Catalyst 34 was 1.5 kg/mm or more.

40 Regarding the active metal content in the Catalyst-34, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of methyl 3-mercapto-propionate used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-34 was 80.9 %.

45

#### EXAMPLE 35: (Method I)

Catalyst-35 was prepared in the same manner as Example 1, except that 75.2 g of thioacetic acid was used as the sulfurizing agent.

50 The breaking strength of the Catalyst-35 was 1.5 kg/mm or more.

Regarding the active metal content in the catalyst-35, molybdenum content was 15 % by weight as  $\text{MoO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The amount of thioacetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-35 was 82.8 %.

55

#### EXAMPLE 36: (Method I)

Catalyst-36 was prepared in the same manner as Example 2, except that 52.3 g of thioacetic acid was used as the sulfurizing agent.

The breaking strength of the Catalyst-36 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-36, tungsten content was 15 % by weight as  $WO_3$  and cobalt content was 4 % by weight as CoO. The amount of thioacetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert W and Co into  $WS_2$  and CoS, respectively.

The desulfurization percentage of the Catalyst-36 was 82.0 %.

#### 10 EXAMPLE 37: (Method II)

Catalyst-37 was prepared in the same manner as Example 3, except that 75.2 g of thioacetic acid was used as the sulfurizing agent.

The breaking strength of the Catalyst-37 was 1.5 kg/mm or more.

15 Regarding the active metal content in the Catalyst-37, molybdenum content was 15 % by weight as  $MoO_3$  and cobalt content was 4 % by weight as CoO. The amount of thioacetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $MoS_2$  and CoS, respectively.

The desulfurization percentage of the Catalyst-37 was 82.3 %.

#### 20 EXAMPLE 38: (Method III)

Catalyst-38 was prepared in the same manner as Example 4, except that 133.6 g of thiobenzoic acid was used as the sulfurizing agent.

25 The breaking strength of the Catalyst-38 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-38, molybdenum content was 15 % by weight as  $MoO_3$  and cobalt content was 4 % by weight as CoO. The amount of thiobenzoic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $MoS_2$  and CoS, respectively.

The desulfurization percentage with the Catalyst-38 was 81.9 %.

#### 30 EXAMPLE 39: (Method IV)

Catalyst-39 was prepared in the same manner as Example 5, except that 78.2 g of thioacetic acid was used as the sulfurizing agent.

35 The breaking strength of the Catalyst-39 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-39, molybdenum content was 15 % by weight as  $MoO_3$ , cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as  $P_2O_5$ . The amount of thioacetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $MoS_2$  and CoS, respectively.

40 The desulfurization percentage with the Catalyst-39 was 83.0 %.

#### EXAMPLE 40: (Method IV)

45 Catalyst-40 was prepared in the same manner as Example 8, except that 78.2 g of thioacetic acid was used as the sulfurizing agent.

The breaking strength of the Catalyst-40 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-40, molybdenum content was 15 % by weight as  $MoO_3$ , cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as  $P_2O_5$ . The amount of thioacetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $MoS_2$  and CoS, respectively.

The desulfurization percentage with the Catalyst-40 was 83.6 %.

#### 55 EXAMPLE 41: (Method IV)

Catalyst-41 was prepared in the same manner as Example 9, except that 139.0 g of thiobenzoic acid

was used as the sulfurizing agent.

The breaking strength of the Catalyst-41 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-41, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of thiobenzoic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoO}$ , respectively.

The desulfurization percentage with the Catalyst-41 was 85.8 %.

#### 10 EXAMPLE 42: (Method IV)

Catalyst-42 was prepared in the same manner as Example 5, except that 139.0 g of thiobenzoic acid was used as the sulfurizing agent.

The breaking strength of the Catalyst-42 was 1.5 kg/mm or more.

15 Regarding the active metal content in the Catalyst-42, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of thiobenzoic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-42 was 83.8 %.

20

#### EXAMPLE 43: (Method IV)

Catalyst-43 was prepared in the same manner as Example 8, except that 139.0 g of thiobenzoic acid was used as the sulfurizing agent.

The breaking strength of the Catalyst-43 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-43, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of thiobenzoic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-43 was 84.2 %.

#### 25 EXAMPLE 44: (Method IV)

Catalyst-44 was prepared in the same manner as Example 13, except that 110.9 g of thioacetic acid was used as the sulfurizing agent.

The breaking strength of the Catalyst-44 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-44, molybdenum content was 20 % by weight as  $\text{MoO}_3$ , nickel content was 4 % by weight as  $\text{NiO}$  and phosphorus content was 6.5 % by weight as  $\text{P}_2\text{O}_5$ . The amount of thioacetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Ni into  $\text{MoS}_2$  and  $\text{NiS}$ , respectively.

The desulfurization percentage with the Catalyst-44 was 80.5 %.

45

#### EXAMPLE 45: (Method V)

Catalyst-45 was prepared in the same manner as Example 13, except that 78.2 g of thioacetic acid was used as the sulfurizing agent.

50 The breaking strength of the Catalyst-45 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-45, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of thioacetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

55 The desulfurization percentage with the Catalyst-45 was 81.5 %.

#### EXAMPLE 46: (Method VI)

Catalyst-46 was prepared in the same manner as Example 14, except that 139.0 g of thiobenzoic acid was used as the sulfurizing agent.

The breaking strength of the Catalyst-46 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-46, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of thiobenzoic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-46 was 83.1 %.

10

#### EXAMPLE 47: (Method VII)

Catalyst-47 was prepared in the same manner as Example 15, except that 78.2 g of thioacetic acid was used as the sulfurizing agent.

15 The breaking strength of the Catalyst-47 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-47, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of thioacetic acid used was 1.1 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

20 The desulfurization percentage with the Catalyst-47 was 82.5 %.

#### EXAMPLE 48: (Method VIII)

25 Catalyst-48 was prepared in the same manner as Example 16, except that 78.2 g of thioacetic acid was used as the sulfurizing agent.

The breaking strength of the Catalyst-48 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-48, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of thioacetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-48 was 82.5 %.

#### 35 EXAMPLE 49: (Method IX)

Catalyst-49 was prepared in the same manner as Example 17, except that 78.2 g of thioacetic acid was used as the sulfurizing agent.

The breaking strength of the Catalyst-49 was 1.5 kg/mm or more.

40 Regarding the active metal content in the Catalyst-49, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of thioacetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-49 was 82.8 %.

45

#### EXAMPLE 50: (Method X)

50 Catalyst-50 was prepared in the same manner as Example 18, except that 78.2 g of thioacetic acid was used as the sulfurizing agent.

The breaking strength of the Catalyst-50 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-50, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of thioacetic acid used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

55 The desulfurization percentage with the Catalyst-50 was 82.5 %.

EXAMPLE 51: (Method I)

Catalyst-51 was prepared in the same manner as Example 1, except that 74.6 g of 2-aminoethanethiol was used as the sulfurizing agent.

5 The breaking strength of the Catalyst-51 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-51, molybdenum content was 15 % by weight as  $\text{MoO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The amount of 2-aminoethanethiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-51 was 81.8 %

10

EXAMPLE 52: (Method I)

15 Catalyst-52 was prepared in the same manner as Example 2, except that 52.1 g of 2-aminoethanethiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-52 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-52, tungsten content was 15 % by weight as  $\text{WO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The amount of 2-aminoethanethiol used was 1.5 times of the theoretical amount of sulfur necessary to convert S and Co into  $\text{SW}_2$  and  $\text{CoS}$ , respectively.

20 The desulfurization percentage with the Catalyst-52 was 81.5 %.

EXAMPLE 53: (Method II)

25 Catalyst-53 was prepared in the same manner as Example 3, except that 74.6 g of 2-aminoethanethiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-53 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-53, molybdenum content was 15 % by weight as  $\text{MoO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The amount of 2-aminoethanethiol used was 1.5 times of the theoretical amount of sulfur necessary for converting Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-53 was 81.5 %.

EXAMPLE 54: (Method III)

35 Catalyst-54 was prepared in the same manner as Example 4, except that 121.2 g of 4-aminothiophenol was used as the sulfurizing agent.

The breaking strength of the Catalyst-54 was 1.5 kg/mm or more.

40 Regarding the active metal content in the Catalyst-54, molybdenum content was 15 % by weight as  $\text{MoO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The 4-aminothiophenol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage of the catalyst 54 was 81.3 %.

45

EXAMPLE 55: (Method IV)

Catalyst-55 was prepared in the same manner as Example 5, except that 77.6 g of 2-aminoethanethiol was used as the sulfurizing agent.

50 The breaking strength of the Catalyst-55 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-55, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 2-aminoethanethiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

55 The desulfurization percentage with the Catalyst-55 was 81.8 %.

EXAMPLE 56: (Method IV)

Catalyst-56 was prepared in the same manner as Example 8, except that 77.6 g of 2-aminoethanethiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-56 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-56, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of 2-aminoethanethiol used was 1.5 times of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-56 was 82.5 %.

10

#### EXAMPLE 57: (Method IV)

Catalyst-57 was prepared in the same manner as Example 9, except that 125.9 g of 4-aminothiophenol was used as the sulfurizing agent.

15 The breaking strength of the Catalyst-57 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-57, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of 4-aminothiophenol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

20 The desulfurization percentage with the Catalyst-57 was 83.8 %.

#### EXAMPLE 58: (Method IV)

25 Catalyst-58 was prepared in the same manner as Example 5, except that 125.9 g of 4-aminothiophenol was used as the sulfurizing agent.

The breaking strength of the Catalyst-58 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-58, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of 4-aminothiophenol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS, respectively.

The desulfurization percentage with the Catalyst-58 was 82.6 %.

#### 35 EXAMPLE 59: (Method IV)

Catalyst-59 was prepared in the same manner as Example 8, except that 125.9 g of 4-aminothiophenol was used as the sulfurizing agent.

The breaking strength of the Catalyst-59 was 1.5 kg/mm or more.

40 Regarding the active metal content in the Catalyst-59, molybdenum content was 15 % by weight as MoO<sub>3</sub>, cobalt content was 4 % by weight as CoO and phosphorus content was 3 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of 4-aminothiophenol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into MoS<sub>2</sub> and CoS.

The desulfurization percentage with the Catalyst-59 was 83.5 %.

45

#### EXAMPLE 60: (Method IV)

50 Catalyst-60 was prepared in the same manner as Example 12, except that 110.1 g of 2-aminoethanethiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-60 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-60, molybdenum content was 20 % by weight as MoO<sub>3</sub>, nickel content was 4 % by weight as NiO and phosphorus content was 6.5 % by weight as P<sub>2</sub>O<sub>5</sub>. The amount of 2-aminoethanethiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Ni to MoS<sub>2</sub> and NiS, respectively.

55 The desulfurization percentage with the Catalyst-60 was 77.8 %.

EXAMPLE 61: (Method V)

Catalyst-61 was prepared in the same manner as Example 13, except that 77.6 g of 2-aminoethanethiol was used as the sulfurizing agent.

5 The breaking strength of the Catalyst-61 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-61, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 2-aminoethanethiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

10 The desulfurization percentage with the Catalyst-61 was 82.0 %.

EXAMPLE 62: (Method VI)

15 Catalyst-62 was prepared in the same manner as Example 14, except that 125.9 g of 4-aminothiophenol was used as the sulfurizing agent.

The breaking strength of the Catalyst-62 was 1.5 kg/mm or more.

Regarding the activemetal content in the Catalyst-62, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 4-aminothiophenol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

20 The desulfurization percentage with the catalyst-62 was 83.2 %.

EXAMPLE 63: (Method VII)

Catalyst-63 was prepared in the same manner as Example 15, except that 77.6 g of 2-aminoethanethiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-63 was 1.5 kg/mm or more.

30 Regarding the active metal content in the Catalyst-63, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 2-aminoethanethiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-63 was 81.8 %.

35

EXAMPLE 64: (Method VIII)

40 Catalyst-64 was prepared in the same manner as Example 16, except that 77.6 g of 2-aminoethanethiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-64 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-64, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 2-aminoethanethiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

45 The desulfurization percentage with the Catalyst-64 was 81.9 %.

EXAMPLE 65: (Method IX)

50 Catalyst-65 was prepared in the same manner as Example 17, except that 77.6 g of 2-aminoethanethiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-65 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-65, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 2-aminoethanethiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-65 was 81.6 %.

EXAMPLE 66: (Method X)

Catalyst-66 was prepared in the same manner as Example 18, except that 77.6 g of 2-aminoethanethiol was used as the sulfurizing agent.

5 The breaking strength of the Catalyst was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-66, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 2-aminoethanethiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

10 The desulfurization percentage with the Catalyst-66 was 81.5 %.

EXAMPLE 67: (Method I)

15 Catalyst-67 was prepared in the same manner as Example 1, except that 45.5 g of ethanedithiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-67 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-67, molybdenum content was 15 % by weight as  $\text{MoO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The amount of ethanedithiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

20 The desulfurization percentage with the Catalyst-67 was 86.0 %.

EXAMPLE 68: (Method I)

25 Catalyst-68 was prepared in the same manner as Example 2, except that 31.8 g of ethanedithiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-68 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-68, tungsten content was 15 % by weight as  $\text{WO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The amount of ethanedithiol used was 1.5 times of the theoretical amount of sulfur necessary to convert W and Co into  $\text{WS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-68 was 84.5 %.

EXAMPLE 69: (Method I)

35 Catalyst-69 was prepared in the same manner as Example 1, except that 76.5 g of 2-mercaptoethanol was used as the sulfurizing agent.

The breaking strength of the Catalyst-69 was 1.5 kg/mm or more.

40 Regarding the active metal content in the Catalyst-69, molybdenum content was 15 % by weight as  $\text{MoO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The amount of 2-mercaptoethanol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-69 was 87.0 %.

EXAMPLE 70: (Method I)

45 Catalyst-70 was prepared in the same manner as Example 2, except that 52.8 g of 2-mercaptoethanol was used as the sulfurizing agent.

50 The breaking strength of the Catalyst-70 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-70, tungsten content was 15 % by weight as  $\text{WO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The amount of 2-mercaptoethanol used was 1.5 times of the theoretical amount of sulfur necessary to convert W and Co into  $\text{WS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-70 was 86.3 %.

55

EXAMPLE 71: (Method II)



Catalyst-71 was prepared in the same manner as Example 3, except that 45.5 g of ethanedithiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-71 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-71, molybdenum content was 15 % by weight as  $\text{MoO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The amount of ethanedithiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-71 was 85.0 %.

#### 10 EXAMPLE 72: (Method II)

Catalyst-72 was prepared in the same manner as Example 3, except that 104.6 g of 3-mercapto-1,2-propanediol was used as the sulfurizing agent.

The breaking strength of the Catalyst-72 was 1.5 kg/mm or more.

15 Regarding the active metal content in the Catalyst-72, molybdenum content was 15 % by weight as  $\text{MoO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The amount of 3-mercapto-1,2-propanediol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-73 was 84.0 %.

20

#### EXAMPLE 73: (Method III)

25 Catalyst-73 was prepared in the same manner as Example 4, except that 59.1 g of 1,4-butanedithiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-73 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-73, molybdenum content was 15 % by weight as  $\text{MoO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The amount of 1,4-butanedithiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

30

The desulfurization percentage with the Catalyst-73 was 83.5 %.

#### EXAMPLE 74: (Method III)

35 Catalyst-74 was prepared in the same manner as Example 4, except that 122.0 g of 4-mercaptophenol was used as the sulfurizing agent.

The breaking strength of the Catalyst-74 was 1.5 kg/mm or more.

40 Regarding the active metal content in the Catalyst-74, molybdenum content was 15 % by weight as  $\text{MoO}_3$  and cobalt content was 4 % by weight as  $\text{CoO}$ . The amount of 4-mercaptophenol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-74 was 84.0 %.

#### EXAMPLE 75: (Method IV)

45

Catalyst-75 was prepared in the same manner as Example 5, except that 47.3 g of ethanedithiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-75 was 1.5 kg/mm or more.

50 Regarding the active metal content in the Catalyst-75, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of ethanedithiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-75 was 87.0 %.

55

#### EXAMPLE 76: (Method IV)

Catalyst-76 was prepared in the same manner as Example 8, except that 61.4 g of 1,4-butanedithiol

was used as the sulfurizing agent.

The breaking strength of the Catalyst-76 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-76, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 1,4-butanedithiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-76 was 86.3 %.

#### 10 EXAMPLE 77: (Method IV)

Catalyst-77 was prepared in the same manner as Example 9, except that 78.6 g of 2-mercaptoethanol was used as the sulfurizing agent.

The breaking strength of the Catalyst-77 was 1.5 kg/mm or more.

15 Regarding the active metal content in the Catalyst-77, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 2-mercaptoethanol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-77 was 88.0 %.

20

#### EXAMPLE 78: (Method IV)

25 Catalyst-78 was prepared in the same manner as Example 5, except that 126.9 g of 4-mercaptophenol was used as the sulfurizing agent.

The breaking strength of the Catalyst-78 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-78, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 4-mercaptophenol used was 1.5 times of the theoretical amount of sulfur necessary to convert 30 Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-78 was 84.8 %.

#### EXAMPLE 79: (Method IV)

35

Catalyst-79 was prepared in the same manner as Example 8, except that 108.9 g of 3-mercapto-1,2-propanediol was used as the sulfurizing agent.

The breaking strength of the Catalyst-79 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-79, molybdenum content was 15 % by weight as 40  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 3-mercapto-1,2-propanediol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-79 was 85.0 %.

45

#### EXAMPLE 80: (Method IV)

Catalyst-80 was prepared in the same manner as Example 12, except that 67.2 g of ethanedithiol was used as the sulfurizing agent.

50 The breaking strength of the Catalyst-80 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-80, molybdenum content was 20 % by weight as  $\text{MoO}_3$ , nickel content was 4 % by weight as  $\text{NiO}$  and phosphorus content was 6.5 % by weight as  $\text{P}_2\text{O}_5$ . The amount of ethanedithiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Ni into  $\text{MoS}_2$  and  $\text{NiS}$ , respectively.

55 The desulfurization percentage of the Catalyst-80 was 83.7 %.

#### EXAMPLE 81: (Method IV)

Catalyst-81 was prepared in the same manner as Example 12, except that 111.6 g of 2-mercaptoethanol was used as the sulfurizing agent.

The breaking strength of the Catalyst-81 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-81, molybdenum content was 20 % by weight as  $\text{MoO}_3$ , nickel content was 4 % by weight as  $\text{NiO}$  and phosphorus content was 6.5 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 2-mercaptoethanol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Ni into  $\text{MoS}_2$  and  $\text{NiS}$ , respectively.

The desulfurization percentage with the Catalyst-81 was 82.0 %.

10

#### EXAMPLE 82: (Method IV)

Catalyst-82 was obtained in the same manner as Example 8, except that 126.9 g of 4-mercaptophenol was used as the sulfurizing agent.

15 The breaking strength of the Catalyst-82 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-82, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 4-mercaptophenol as used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

20 The desulfurization percentage with the Catalyst-82 was 86.7 %.

#### EXAMPLE 83: (Method IV)

25 Catalyst-83 was prepared in the same manner as Example 8, except that 78.6 g of 2-mercaptoethanol was used as the sulfurizing agent.

The breaking strength of the catalyst-83 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-83, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ .

30 The amount of 2-mercaptoethanol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-83 was 87.6 %.

#### EXAMPLE 84: (Method IV)

Catalyst-84 was prepared in the same manner as Example 8, except that 47.3 g of ethanedithiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-84 was 1.5 kg/mm or more.

40 Regarding the active metal content in the Catalyst-84, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of ethanedithiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-84 was 89.5 %.

45

#### EXAMPLE 85: (Method V)

Catalyst-85 was prepared in the same manner as Example 13, except that 47.3 g of ethanedithiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-85 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-85, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of ethanedithiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and

55 Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-85 was 88.0 %.

EXAMPLE 85: (Method V)

Catalyst-86 was prepared in the same manner as Example 13, except that 78.6 g of 2-mercaptoethanol was used as the sulfurizing agent.

5 The breaking strength of the Catalyst-86 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst 86, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 2-mercaptoethanol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

10 The desulfurization percentage with the Catalyst-86 was 85.0 %.

EXAMPLE 87: (Method VI)

15 Catalyst-87 was prepared in the same manner as Example 14, except that 61.4 g of 4-butanedithiol was used as the sulfurizing agent.

The breaking strength of the Catalyst-87 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-87, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 4-butanedithiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-87 was 85.3 %.

EXAMPLE 88: (Method VII)

Catalyst-88 was prepared in the same manner as Example 15, except that 108.9 g of 3-mercapto-1,2-propanediol was used as the sulfurizing agent.

The breaking strength of the Catalyst-88 was 1.5 kg/mm or more.

30 Regarding the active metal content in the Catalyst-88, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 3-mercapto-1,2-propanediol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-88 was 83.8 %.

35

EXAMPLE 89: (Method VIII)

40 Catalyst-89 was prepared in the same manner as Example 16, except that 126.9 g of 4-mercaptophenol was used as the sulfurizing agent.

The breaking strength of the Catalyst-89 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-89, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 4-mercaptophenol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-89 was 84.8 %.

EXAMPLE 90: (Method IX)

50

Catalyst-90 was prepared in the same manner as Example 17, except that 78.6 g of 2-mercaptoethanol was used as the sulfurizing agent.

The breaking strength of the Catalyst-90 was 1.5 kg/mm or more.

Regarding the active metal content in the catalyst-90, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of 2-mercaptoethanol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

The desulfurization percentage with the Catalyst-90 was 84.5 %.

EXAMPLE 91: (Method X)

Catalyst-91 was prepared in the same manner as Example 18, except that 47.3 g of ethanedithiol was used as the sulfurizing agent.

5 The breaking strength of the Catalyst-91 was 1.5 kg/mm or more.

Regarding the active metal content in the Catalyst-91, molybdenum content was 15 % by weight as  $\text{MoO}_3$ , cobalt content was 4 % by weight as  $\text{CoO}$  and phosphorus content was 3 % by weight as  $\text{P}_2\text{O}_5$ . The amount of ethanedithiol used was 1.5 times of the theoretical amount of sulfur necessary to convert Mo and Co into  $\text{MoS}_2$  and  $\text{CoS}$ , respectively.

10 The desulfurization percentage with the Catalyst-91 was 87.0 %.

COMPARATIVE EXAMPLE 1:

15 A commercial catalyst comprising 15 wt.% of  $\text{MoO}_3$  and 4 wt.% of  $\text{CoO}$  as carried on  $\gamma$ -alumina (KF-742, commercial product by Nippon Ketjen Co.) was prepared.

The catalyst was presulfurized in accordance with the following condition:

Sulfurizing Oil:

3 wt.% n-butylmercaptan/Kuwait Straight-run light gas oil

20 Amount of Catalyst:

3 ml

Raw Material Oil Liquid Hourly Space Velocity:

$2.0 \text{ hr}^{-1}$

Reaction Pressure (Hydrogen Pressure):

25  $30 \text{ kg/cm}^2$

Reaction Temperature:

$316^\circ \text{C}$

Hydrogen/Oil Ratio:

300 N liter/liter

30 Oil Passing Time:

8hr

The activity of the thus presulfurized catalyst was evaluated in the same manner as in the above-mentioned examples. As a result, the desulfurization percentage was 82.4 %.

35

COMPARATIVE EXAMPLE 2:

100 g of shaped  $\gamma$ -alumina carrier having a relative surface area of  $280 \text{ m}^2/\text{g}$  and a pore volume of  $0.75 \text{ ml/g}$  was impregnated with 80 ml of a processing liquid prepared from 19.2 g of molybdenum trioxide, 8.2 g of cobalt carbonate having Co-content of 49.1 wt.%, 6.2 g of 85 wt.% phosphoric acid and water and dried at  $110^\circ \text{C}$  for 16 hours and thereafter fired at  $500^\circ \text{C}$  for 2 hours. Accordingly, a catalyst containing 15 % by weight of  $\text{MoO}_3$ , 4 % by weight of  $\text{CoO}$  and 3 % by weight of  $\text{P}_2\text{O}_5$  was obtained.

The catalyst was presulfurized in the same manner as in the above-mentioned Comparative Example 1 and the activity of the thus presulfurized catalyst was evaluated in the same manner as in the above-mentioned examples. As a result, the desulfurization percentage was 80.4 %.

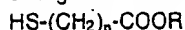
45 It takes about 8 hours or so to presulfurize the conventional catalysts. In the case of the catalyst disclosed in the above-mentioned Japanese Patent Publication No. 61-111144 must be fired for at least 1 hour after it was impregnated with a sulfurizing agent. As opposed to them, the catalysts of the present invention require neither presulfurization nor firing and can directly be applied to hydrotreatment, as they are prepared by the use of an organic compound having one or two sulfurs as a sulfurizing agent. Accordingly, the catalysts of the present invention are more economical than the conventional catalysts.

50 While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

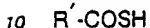
55

## Claims

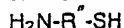
1. A catalyst for hydrotreating hydrocarbons, which comprises a shaped body of a mixture composed of a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium, at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table and at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:



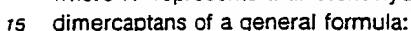
where n represents an integer of from 1 to 3; and R represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, thio-acids of a general formula:



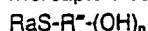
where R' represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, amino-substituted mercaptans of a general formula:



where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, dimercaptans of a general formula:



where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, and mercapto-alcohols of a general formula:



- where R'' represents an alkyl group having from 1 to 15 carbon atoms, or a phenyl group; Ra represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and n represents an integer of from 1 to 2.

2. The catalyst for hydrotreating hydrocarbons as claimed in claim 1, in which the oxide of aluminium and/or oxide hydrate of aluminium for constituting the carrier substance is(are) at least one selected from  $\gamma$ -alumina, dehydrated boehmite and spray-dried boehmite.

3. The catalyst for hydrotreating hydrocarbons as claimed in claim 1, in which the water-soluble compounds of metals of Group VI of the Periodic Table are at least one selected from ammonium molybdate and ammonium tungstate, and ammonium molybdate and ammonium tungstate as prepared by treating molybdenum trioxide and tungsten trioxide, respectively, with ammonia gas; and the water-soluble compounds of metals of Group VIII of the Periodic Table are at least one selected from cobalt nitrate, cobalt carbonate, nickel nitrate and nickel carbonate; the mixture of constituting the shaped body containing at least one selected from the said water-soluble compounds.

4. The catalyst for hydrotreating hydrocarbons as claimed in claim 1, in which the mercapto-carboxylic acids of a general formula:



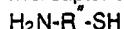
- where n represents an integer of from 1 to 3; and R represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, are at least one selected from mercapto-acetic acid and  $\beta$ -mercapto-propionic acid and alkali metal salts, alkaline earth metal salts and ammonium salts thereof and methyl mercapto-acetate, ethyl 2-mercapto-acetate, 2-ethylhexyl mercapto-acetate and methyl 3-mercapto-propionate.

5. The catalyst for hydrotreating hydrocarbons as claimed in claim 1, in which the thio-acids of a general formula:



- where R' represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, are at least one selected from thio-acetic acid and thio-benzoic acid.

6. The catalyst for hydrotreating hydrocarbons as claimed in claim 1, in which the amino-substituted mercaptans of a general formula:



- where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, are at least one selected from 2-aminoethanethiol and 4-aminothiophenol.

7. The catalyst for hydrotreating hydrocarbons as claimed in claim 1, in which the dimercaptans of a general formula:



- where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, are at least one selected from ethanedithiol and 1,4-butanedithiol.

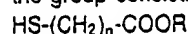
8. The catalyst for hydrotreating hydrocarbons as claimed in claim 1, in which the mercapto-alcohols of a general formula:



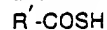
where R<sup>m</sup> represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group; Ra represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and n represents an integer of from 1 to 2, are at least one selected from 2-mercaptoethanol, 2-(methylthio)ethanol, 2-(ethylthio)ethanol, 3-mercapto-2-butanol, 4-mercaptophenol, 2-(methylthio)phenol, 4-(methylthio)phenol, 2-(ethylthio)phenol, 3-mercapto-1,2-propanediol, 3-methylthio-1,2-propanediol and 3-ethylthio-1,2-propanediol.

9. The catalyst for hydrotreating hydrocarbons as claimed in claim 1, in which the content of the metals of the Groups VI and VIII of the Periodic Table is from 1 to 30 % by weight as the metal oxide, when the catalyst contains one metal of them, or the content of the metal of Group VI is from 5 to 30 % by weight as the metal oxide and that of the metal of Group VIII is from 1 to 8 % by weight as the metal oxide when the catalyst contains both the metals of Groups VI and VIII.

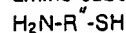
10. A method for preparing a catalyst for hydrotreating hydrocarbons, which is characterized in that a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with a solution containing at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table and at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:



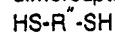
where n represents an integer of from 1 to 3; and R represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, thio-acids of a general formula:



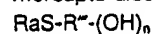
where R' represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, amino-substituted mercaptans of a general formula:



where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, dimercaptans of a general formula:



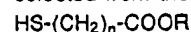
where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, and mercapto-alcohols of a general formula:



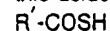
where R<sup>m</sup> represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group; Ra represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and n represents an integer of from 1 to 2,

and the resulting blend is shaped and dried to prepare the said catalyst.

11. A method for preparing a catalyst for hydrotreating hydrocarbons, which is characterized in that a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with an aqueous solution of at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table, the resulting blend is shaped and then temporarily dried, and the thus dried shaped body is impregnated with a solution of at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:



where n represents an integer of from 1 to 3; and R represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, thio-acids of a general formula:



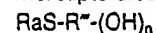
where R' represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, amino-substituted mercaptans of a general formula:



where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, dimercaptans of a general formula:



where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, and mercapto-alcohols of a general formula:

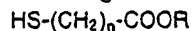


where R<sup>m</sup> represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group; Ra represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and n represents an integer of from 1 to 2,

and then again dried to prepare the said catalyst.

12. A method for preparing a catalyst for hydrotreating hydrocarbon, which is characterized in that a

carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with an aqueous solution of at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:

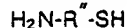


- 5 where  $n$  represents an integer of from 1 to 3; and  $R$  represents a hydrogen atom, an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, thio-acids of a general formula:



where  $R'$  represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms,

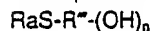
- 10 amino-substituted mercaptans of a general formula:



where  $R''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, dimercaptans of a general formula:



- 15 where  $R''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, and mercapto-alcohols of a general formula:



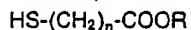
where  $R''$  represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group;  $R_a$  represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and  $n$  represents an integer of from 1 to 2,

20 the resulting blend is shaped and then temporarily dried, and the thus dried shaped body is impregnated with an aqueous solution of at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table, and then again dried to prepare the said catalyst.

13. The method for preparing a catalyst for hydrogenation of hydrocarbons as claimed in anyone of claims 10 to 12, in which the oxide of aluminium and/or oxide hydrate of aluminium for constituting the carrier substance is(are) at least one selected from  $\gamma$ -alumina, dehydrated boehmite and spray-dried boehmite.

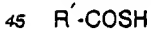
14. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 10 to 12, in which the water-soluble compounds of metals of Group VI of the Periodic Table are at least one selected from ammonium molybdate and ammonium tungstate, and ammonium molybdate and ammonium tungstate as prepared by treating molybdenum trioxide and tungsten trioxide, respectively, with ammonia gas; and the water-soluble compounds of metals of Group VIII of the Periodic Table are at least one selected from cobalt nitrate, cobalt carbonate, nickel nitrate and nickel carbonate; the said aqueous solution containing at least one selected from the said water-soluble compounds.

- 35 15. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 10 to 12, in which the mercapto-carboxylic acids of a general formula:



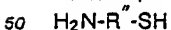
- 40 where  $n$  represents an integer of from 1 to 3; and  $R$  represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, are at least one selected from mercapto-acetic acid and  $\beta$ -mercapto-propionic acid and alkali metal salts, alkaline earth metal salts and ammonium salts thereof and methyl mercapto-acetate, ethyl 2-mercapto-acetate, 2-ethylhexyl mercapto-acetate and methyl 3-mercapto-propionate.

16. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 10 to 12, in which the thio-acids of a general formula:



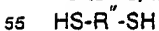
where  $R'$  represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, are at least one selected from thio-acetic acid and thio-benzoic acid.

17. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 10 to 12, in which the amino-substituted mercaptans of a general formula:



where  $R''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, are at least one selected from 2-aminoethanethiol and 4-aminothiophenol.

18. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 10 to 12, in which the dimercaptans of a general formula:



where  $R''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, are at least one selected from ethanedithiol and 1,4-butanedithiol.

19. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims



10 to 12, in which the mercapto-alcohols of a general formula:



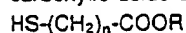
where R<sup>n</sup> represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group; Ra represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and n represents an integer of from 1 to 2, are at least one selected from 2-mercaptoethanol, 2-(methylthio)ethanol, 2-(ethylthio)ethanol, 3-mercapto-2-butanol, 4-mercaptoethanol, 2-(methylthio)phenol, 4-(methylthio)phenol, 2-(ethylthio)phenol, 3-mercapto-1,2-propanediol, 3-methylthio-1,2-propanediol and 3-ethylthio-1,2-propanediol.

20. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 10 to 12, in which the content of the metals of Groups VI and VIII of the Periodic Table in the catalyst is from 1 to 30 % by weight as the metal oxide, when the catalyst contains one metal of them, or the content of the metal of Group VI in the catalyst is from 5 to 30 % by weight as the metal oxide and that of the metal of Group VIII therein is from 1 to 8 % by weight as the metal oxide when the catalyst contains both the metals of Groups VI and VIII.

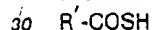
21. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 10 to 12, in which the amount of the mercapto-carboxylic acids and other sulfurizing agents is from 1 to 3 equivalent times of the amount of the sulfur necessary for forming sulfides of the metals of Groups VI and VIII of the Periodic Table, the said sulfides being high active in hydrogenation reaction.

22. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 10 to 12, in which the drying temperature falls within the scope of from 50 to 200 °C and the drying time falls within the scope of from 2 to 20 hours.

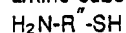
23. A catalyst for hydrotreating hydrocarbons, which comprises a shaped body of a mixture composed of a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium, at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table, phosphoric acid and at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:



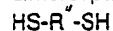
where n represents an integer of from 1 to 3; and R represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, thio-acids of a general formula:



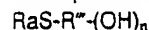
where R' represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, amino-substituted mercaptans of a general formula:



where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, dimercaptans of a general formula:



where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, and mercapto-alcohols of a general formula:

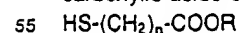


where R<sup>n</sup> represents an alkyl group having from 1 to 15 carbon atoms, or a phenyl group; Ra represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and n represents an integer of from 1 to 2.

24. The catalyst for hydrotreating hydrocarbons as claimed in claim 23, in which the oxide of aluminium and/or oxide hydrate of aluminium for constituting the carrier substance is(are) at least one selected from γ-alumina, dehydrated boehmite and spray-dried boehmite.

25. The catalyst for hydrotreating hydrocarbons as claimed in claim 23, in which the water-soluble compounds of metals of Group VI of the Periodic Table are at least one selected from ammonium molybdate and ammonium tungstate, and ammonium molybdate and ammonium tungstate as prepared by treating molybdenum trioxide and tungsten trioxide, respectively, with ammonia gas; and the water-soluble compounds of metals of Group VIII of the Periodic Table are at least one selected from cobalt nitrate, cobalt carbonate, nickel nitrate and nickel carbonate; the mixture of constituting the shaped body containing at least one selected from the said water-soluble compounds.

26. The catalyst for hydrotreating hydrocarbons as claimed in claim 23, in which the mercapto-carboxylic acids of a general formula:



where n represents an integer of from 1 to 3; and R represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, an alkyl group having from 1 to 10 carbon atoms, are at least one selected from mercapto-acetic acid and β-mercapto-propionic acid and alkali metal salts, alkaline earth

metta salts and ammonium salts thereof and methyl mercapto-acetate, ethyl 2-mercapto-acetate, 2-ethylhexyl mercapto-acetate and methyl 3-mercapto-propionate.

27. The catalyst for hydrotreating hydrocarbons as claimed in claim 23, in which the thio-acids of a general formula:

5  $R'-COSH$

where  $R'$  represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, are at least one selected from thio-acetic acid and thio-benzoic acid.

28. The catalyst for hydrotreating hydrocarbons as claimed in claim 23, in which the amino-substituted mercaptans of a general formula:

10  $H_2N-R''-SH$

where  $R''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, are at least one selected from 2-aminoethanethio and 4-aminothiophenol.

29. The catalyst for hydrotreating hydrocarbons as claimed in claim 23, in which the dimercaptans of a general formula:

15  $HS-R'''-SH$

where  $R'''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, are at least one selected from ethanedithiol and 1,4-butanedithiol.

30. The catalyst for hydrotreating hydrocarbons as claimed in claim 23, in which the mercapto-alcohols of a general formula:

20  $RaS-R''-(OH)_n$

where  $R''$  represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group;  $R_a$  represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and  $n$  represents an integer of from 1 to 2, are at least one selected from 2-mercaptoethanol, 2-(methylthio)ethanol, 2-(ethylthio)ethanol, 3-mercapto-2-butanol, 4-mercaptothiophenol, 2-(methylthio)phenol, 4-(methylthio)phenol, 2-(ethylthio)phenol, 3-mercapto-1,2-propanediol, 3-methylthio-1,2-propanediol and 3-ethylthio-1,2-propanediol.

31. The catalyst for hydrotreating hydrocarbons as claimed in claim 23, in which the content of the metals of the Groups VI and VIII of the Periodic Table is from 1 to 30 % by weight as the metal oxide, When the catalyst contains one metal of them, or the content of the metal of Group VI is from 5 to 30 % by weight as the metal oxide and that of the metal of Group VIII is from 1 to 8 % by weight as the metal oxide

30 when the catalyst contains both the metals of Groups VI and VIII.

32. A method for preparing a catalyst for hydrotreating hydrocarbons, which is characterized in that a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with a solution containing at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table, phosphoric acid and at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:

35  $HS-(CH_2)_n-COOR$

where  $n$  represents an integer of from 1 to 3; and  $R$  represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, thio-acids of a general formula:

40  $R'-COSH$

where  $R'$  represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, amino-substituted mercaptans of a general formula:

$H_2N-R''-SH$

where  $R''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms,

45 dimercaptans of a general formula:

$HS-R'''-SH$

where  $R'''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, and mercapto-alcohols of a general formula:

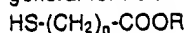
$RaS-R''-(OH)_n$

50 where  $R''$  represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group;  $R_a$  represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and  $n$  represents an integer of from 1 to 2,

and the resulting blend is shaped and dried to prepare the said catalyst.

33. A method for preparing a catalyst for hydrotreating hydrocarbons, which is characterized in that a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with an aqueous solution comprising at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table and phosphoric acid, the resulting blend is shaped and then temporarily dried, and the thus dried shaped body is impregnated with a solution

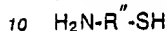
of at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:



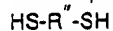
where n represents an integer of from 1 to 3; and R represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, thio-acids of a general formula:



where R' represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, amino-substituted mercaptans of a general formula:

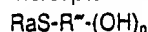


where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, dimercaptans of a general formula:



where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, and

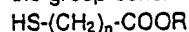
mercapto-alcohols of a general formula:



where R'' represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group; Ra represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and n represents an integer of from 1 to 2,

and then again dried to prepare the said catalyst.

34. A method for preparing a catalyst for hydrotreating hydrocarbons, which is characterized in that a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with a solution comprising at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table and at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:



where n represents an integer of from 1 to 3; and R represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, thio-acids of a general formula:

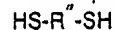


where R' represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, amino-substituted mercaptans of a general formula:



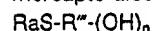
where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms,

dimercaptans of a general formula:



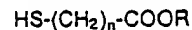
where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, and

mercapto-alcohols of a general formula:

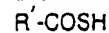


where R'' represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group; Ra represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and n represents an integer of from 1 to 2, the resulting blend is shaped and temporarily dried, and the thus dried shaped body is impregnated with an aqueous solution of phosphoric acid, and then again dried to prepare the said catalyst.

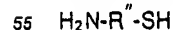
35. A method for preparing a catalyst for hydrotreating hydrocarbons, which is characterized in that a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with a solution comprising phosphoric acid and at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:



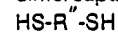
where n represents an integer of from 1 to 3; and R represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, thio-acids of a general formula:



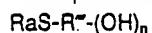
where R' represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, amino-substituted mercaptans of a general formula:



where R'' represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, dimercaptans of a general formula:

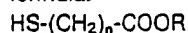


where  $R''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, and mercapto-alcohols of a general formula:

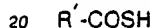


where  $R''$  represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group;  $Ra$  represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and  $n$  represents an integer of from 1 to 2, the resulting blend is shaped and temporarily dried, and the thus dried shaped body is impregnated with an aqueous solution containing at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table, and then again dried to prepare the said catalyst.

36. A method for preparing a catalyst for hydrotreating hydrocarbons, which is characterized in that a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with an aqueous solution of at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table, the resulting blend is shaped and temporarily dried, and the thus dried shaped body is impregnated with a solution comprising phosphoric acid and at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:



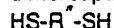
where  $n$  represents an integer of from 1 to 3; and  $R$  represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, thio-acids of a general formula:



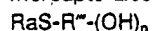
where  $R'$  represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, amino-substituted mercaptans of a general formula:



where  $R''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, dimercaptans of a general formula:

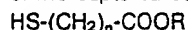


where  $R''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, and mercapto-alcohols of a general formula:



where  $R''$  represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group;  $Ra$  represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and  $n$  represents an integer of from 1 to 2, and then again dried to prepare the said catalyst.

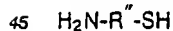
37. A method for preparing a catalyst for hydrotreating hydrocarbons, which is characterized in that a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is blended and kneaded with a solution of at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:



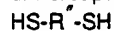
where  $n$  represents an integer of from 1 to 3; and  $R$  represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, thio-acids of a general formula:



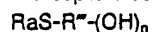
where  $R'$  represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, amino-substituted mercaptans of a general formula:



where  $R''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, dimercaptans of a general formula:



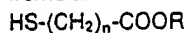
where  $R''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, and mercapto-alcohols of a general formula:



where  $R''$  represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group;  $Ra$  represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and  $n$  represents an integer of from 1 to 2, the resulting blend is shaped and temporarily dried, and the thus dried shaped body is impregnated with an aqueous solution comprising at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table, and phosphoric acid, and then again dried to prepare the said catalyst.

38. A method for preparing a catalyst for hydrotreating hydrocarbons, which is characterized in that a carrier substance consisting essentially of an oxide of aluminium and/or an oxide hydrate of aluminium is

blended and kneaded with an aqueous solution of phosphoric acid, the resulting blend is shaped and temporarily dried, and the thus dried shaped body is impregnated with a solution comprising at least one selected from water-soluble compounds of metals of Group VI and Group VIII of the Periodic Table and at least one organic compound selected from the group consisting of mercapto-carboxylic acids of a general formula:

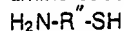


where  $n$  represents an integer of from 1 to 3; and  $R$  represents a hydrogen atom, an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms,

thio-acids of a general formula:

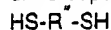


where  $\text{R}'$  represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, amino-substituted mercaptans of a general formula:

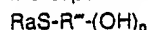


where  $\text{R}''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms,

dimercaptans of a general formula:



where  $\text{R}''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, and mercapto-alcohols of a general formula:



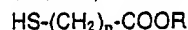
where  $\text{R}''$  represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group;  $\text{Ra}$  represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and  $n$  represents an integer of from 1 to 2,

and then again dried to prepare the said catalyst.

39. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 32 to 38, in which the oxide of aluminium and/or oxide hydrate of aluminium for constituting the carrier substance is(are) at least one selected from  $\gamma$ -alumina, dehydrated boehmite and spray-dried boehmite.

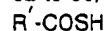
40. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 32 to 38, in which the water-soluble compounds of metals of Group VI of the Periodic Table are at least one selected from ammonium molybdate and ammonium tungstate, and ammonium molybdate and ammonium tungstate as prepared by treating molybdenum trioxide and tungsten trioxide, respectively, with ammonia gas; and the water-soluble compounds of metals of Group VIII of the Periodic Table are at least one selected from cobalt nitrate, cobalt carbonate, nickel nitrate and nickel carbonate; the said aqueous solution containing at least one selected from the said water-soluble compounds.

41. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 32 to 38, in which the mercapto-carboxylic acids of a general formula:



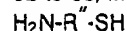
where  $n$  represents an integer of from 1 to 3; and  $R$  represents a hydrogen atom, or an alkali metal, an alkaline earth metal, an ammonium group, or an alkyl group having from 1 to 10 carbon atoms, are at least one selected from mercapto-acetic acid and  $\beta$ -mercapto-propionic acid and alkali metal salts, alkaline earth metal salts and ammonium salts thereof and methyl mercapto-acetate, ethyl 2-mercapto-acetate, 2-ethylhexyl mercapto-acetate and methyl 3-mercapto-propionate.

42. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 32 to 38, in which the thio-acids of a general formula:



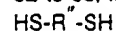
where  $\text{R}'$  represents a monovalent hydrocarbon group having from 1 to 15 carbon atoms, are at least one selected from thio-acetic acid and thio-benzoic acid.

43. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 32 to 38, in which the amino-substituted mercaptans of a general formula:



where  $\text{R}''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, are at least one selected from 2-aminoethanethiol and 4-aminothiophenol

44. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 32 to 38, in which the dimercaptans of a general formula:



where  $\text{R}''$  represents a divalent hydrocarbon group having from 1 to 15 carbon atoms, are at least one selected from ethanedithiol and 1,4-butanedithiol.

45. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 32 to 38, in which the mercapto-alcohols of a general formula:

$\text{RaS-R}''\text{-(OH)}_n$

where  $\text{R}''$  represents an alkyl group having from 1 to 15 carbon atoms or a phenyl group; Ra represents a hydrogen atom or an alkyl group having from 1 to 2 carbon atoms; and n represents an integer of from 1 to 2, are at least one selected from 2-mercaptoethanol, 2-(methylthio)ethanol, 2-(ethylthio)ethanol, 3-mercapto-  
 5 2-butanol, 4-mercaptophenol, 2-(methylthio)phenol, 4-(methylthio)phenol, 3-mercapto-1,2-propanediol, 3-methylthio-1,2-propanediol and 3-ethylthio-1,2-propanediol.

46. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 32 to 38, in which the content of the metals of Groups VI and VIII of the Periodic Table in the catalyst is from 1 to 30 % by weight as the metal oxide, when the catalyst contains one metal of them, or the content  
 10 of the metal of Group VI in the catalyst is from 5 to 30 % by weight as the metal oxide and that of the metal of Group VIII therein is from 1 to 8 by weight as the metal oxide when the catalyst contains both the metals of Groups VI and VIII.

47. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 32 to 38, in which the amount of the mercapto-carboxylic acids and other sulfurizing agents is from 1 to 3  
 15 equivalent times of the amount of the sulfur necessary for forming sulfides of the metals of Groups VI and VIII of the Periodic Table, the said sulfides being high active in hydrogenation reaction.

48. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims 32 to 38, in which the amount of the phosphoric acid is about 3 % by weight or so as  $\text{P}_2\text{O}_5$

49. The method for preparing a catalyst for hydrotreating hydrocarbons as claimed in anyone of claims  
 20 32 to 38, in which the drying temperature falls within the range of from 50 to 200 °C and the drying time falls within the range of from 2 to 20 hours.

25

30

35

40

45

50

55